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(54) **METHOD OF PRODUCING FIBER AND FILM OF SILK AND SILK-LIKE MATERIAL**

Publication Classification

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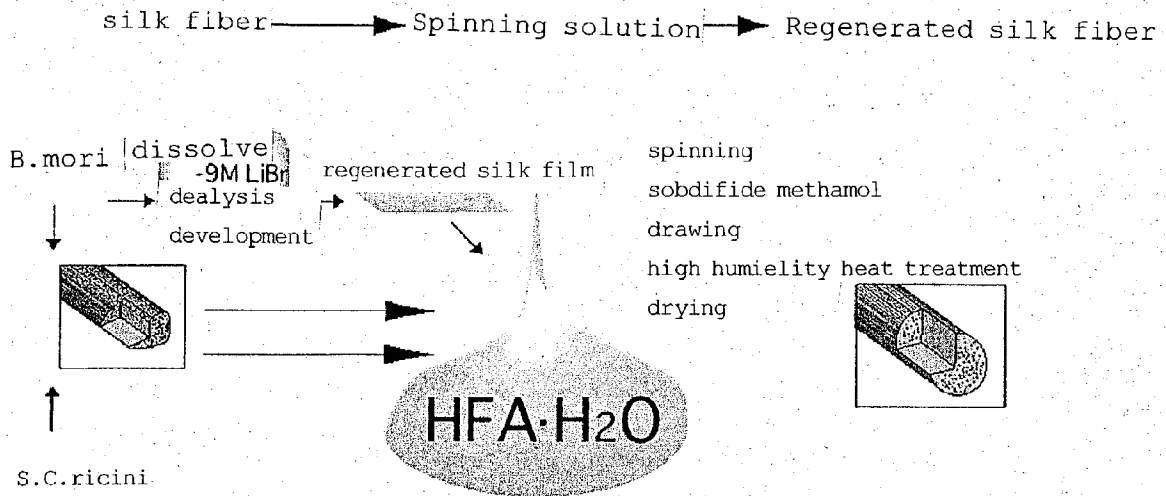
ABSTRACT

A method of manufacturing silk or silk-like fibers materials, wherein a solution wherein silk fibroins and/or silk-like materials are dissolved in hexafluoroacetone hydrate, is spun and extended if necessary, and a method of manufacturing a silk or silk-like film wherein a solution in which silk fibroins and/or silk-like materials are dissolved in hexafluoroacetone hydrate, developed, and extended after drying if necessary.

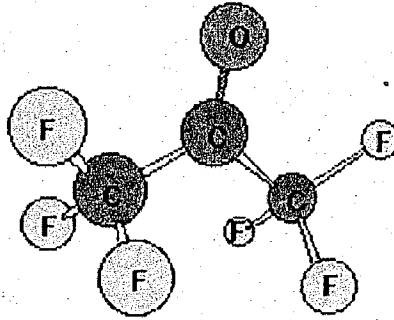
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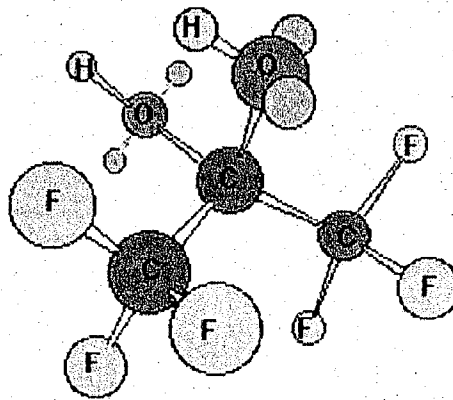
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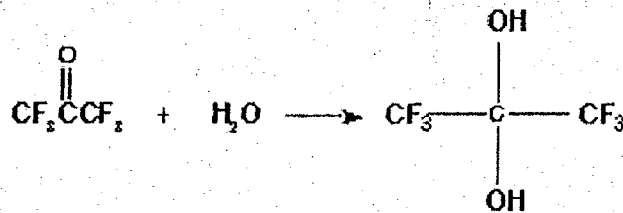
A



B



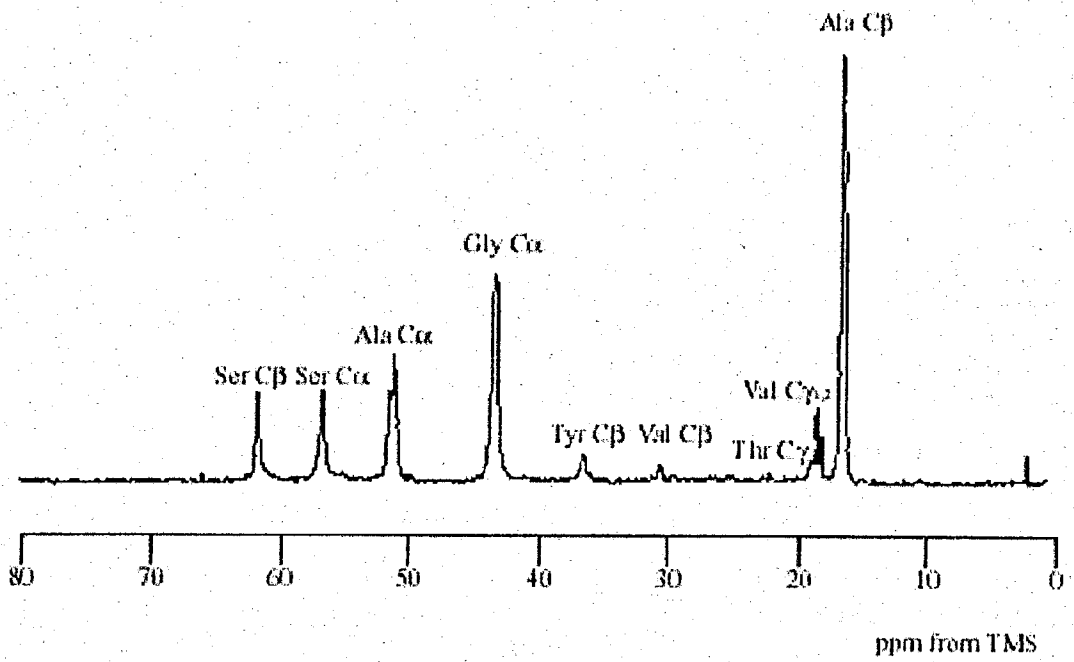
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A:Hexafluoroacetone,B:An atomic model diagram of gen-diol type Hexafluoroacetone,C:Reaction equation of the above reaction.¹⁾

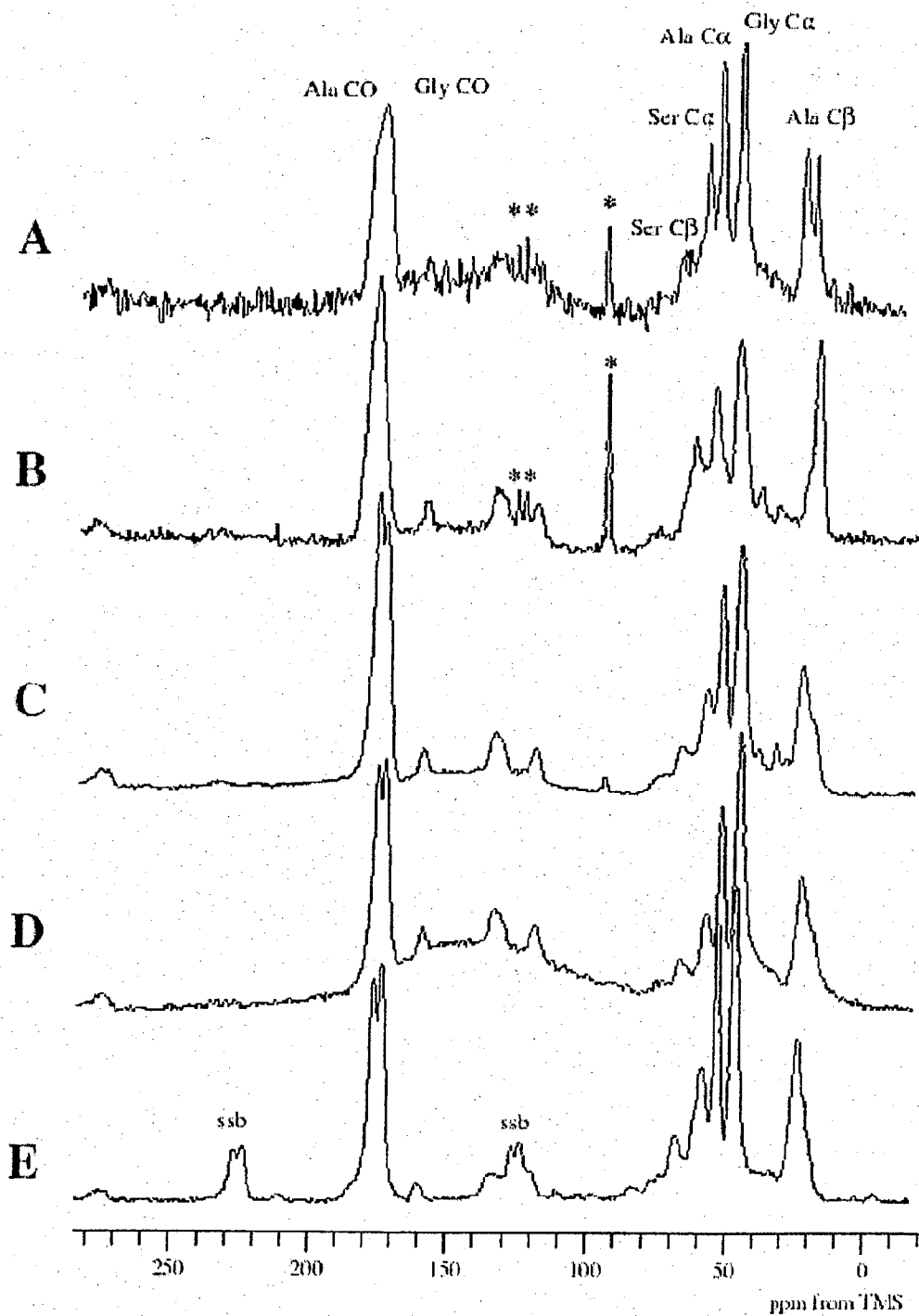
1) W. J. Middleton, R. V. Lindsey Jr., *Journal of American Chemical Society*, 86, 4948-4952 (1964)

Figure 1



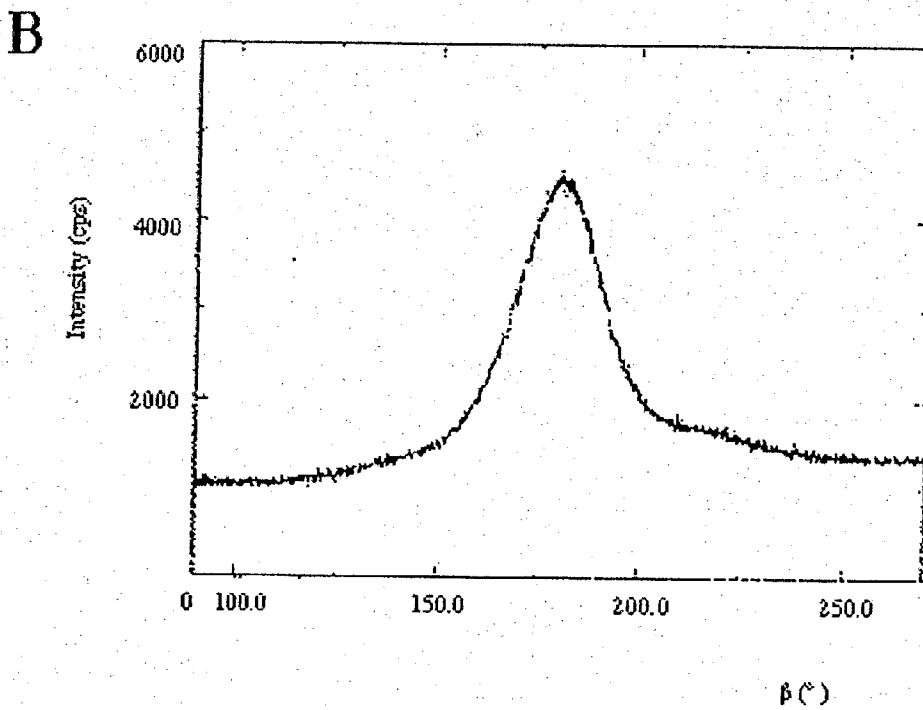
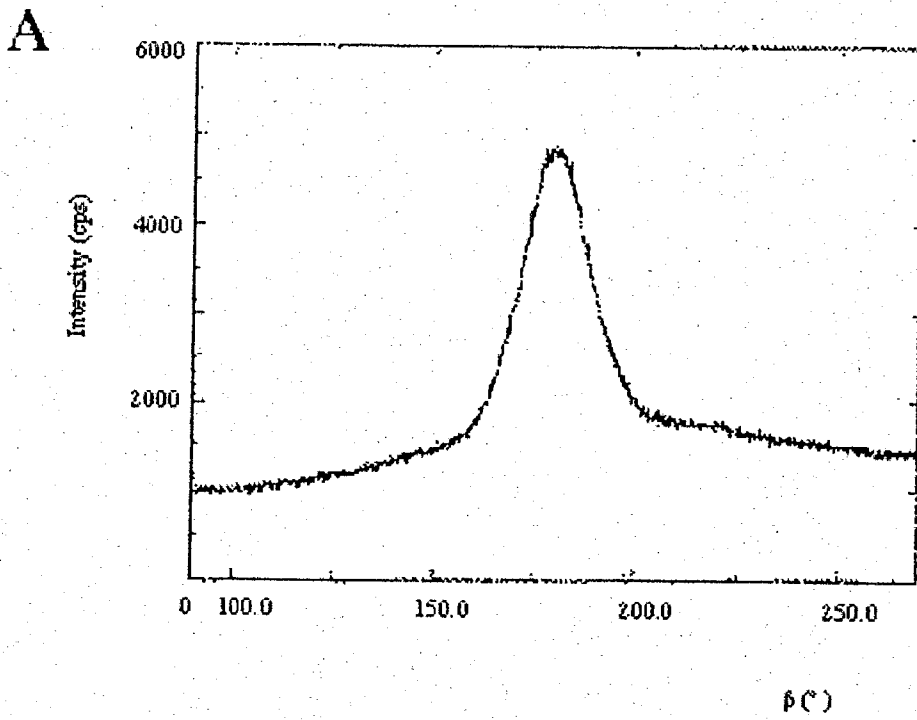
A $C\alpha, C\beta$ region soluble ¹³C NMR spectrum of B.mori fibroins in HFA hydrate.

Figure 2



- A: A material obtained by drying the dissolved B.mori fibers after an addition of HFA hydrate.
- B: A film obtained from now solution for spinning.
- C: A regenerated undrawn silk fiber.
- D: A regenerated B.mori silk fiber.
- E: B.mori silk fiber.

Figure 3



A: A regenerated silk fiber obtained from HFA system.
 B: Direction strength of *B. mori* silk fiber.

Figure 4

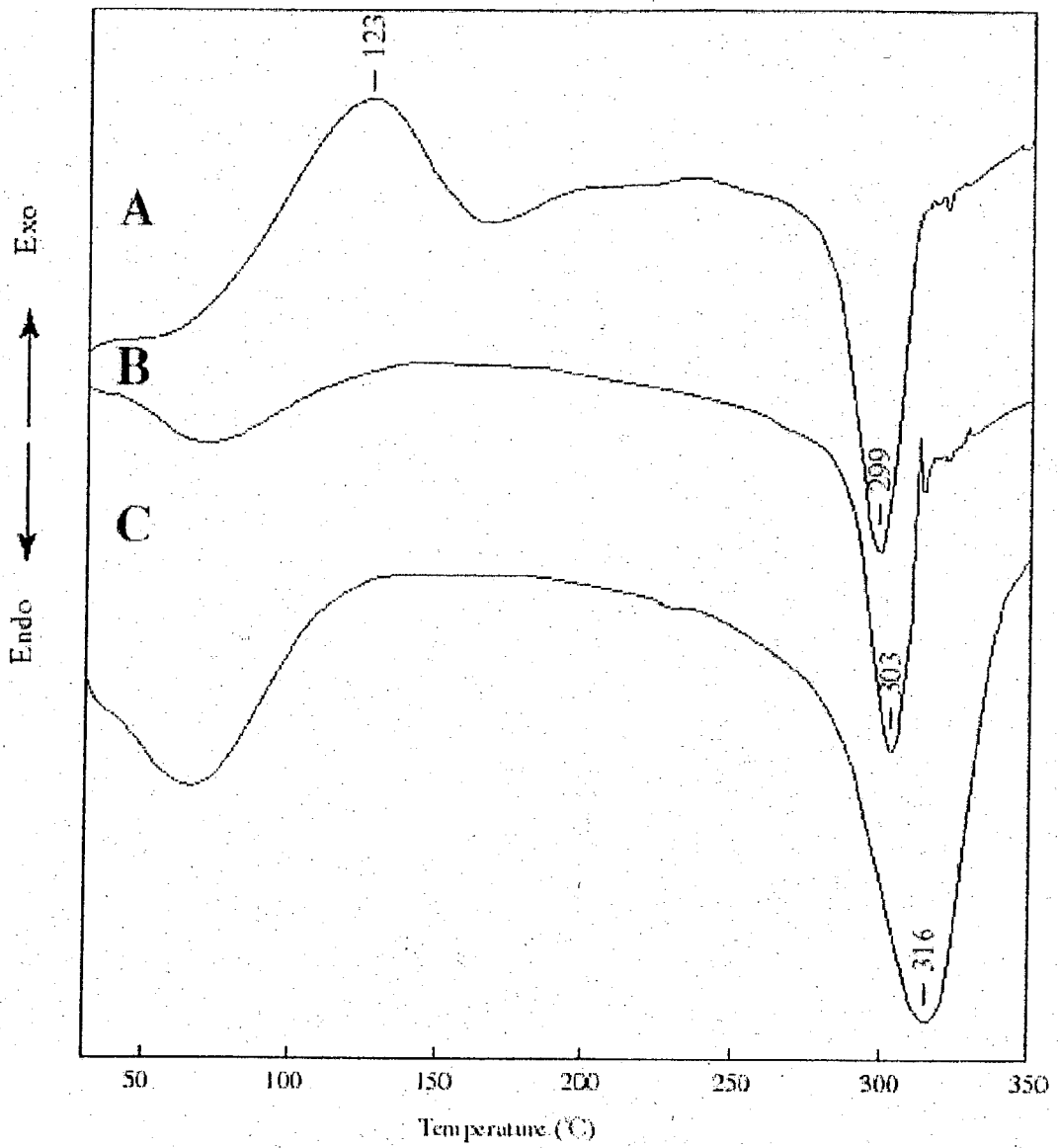
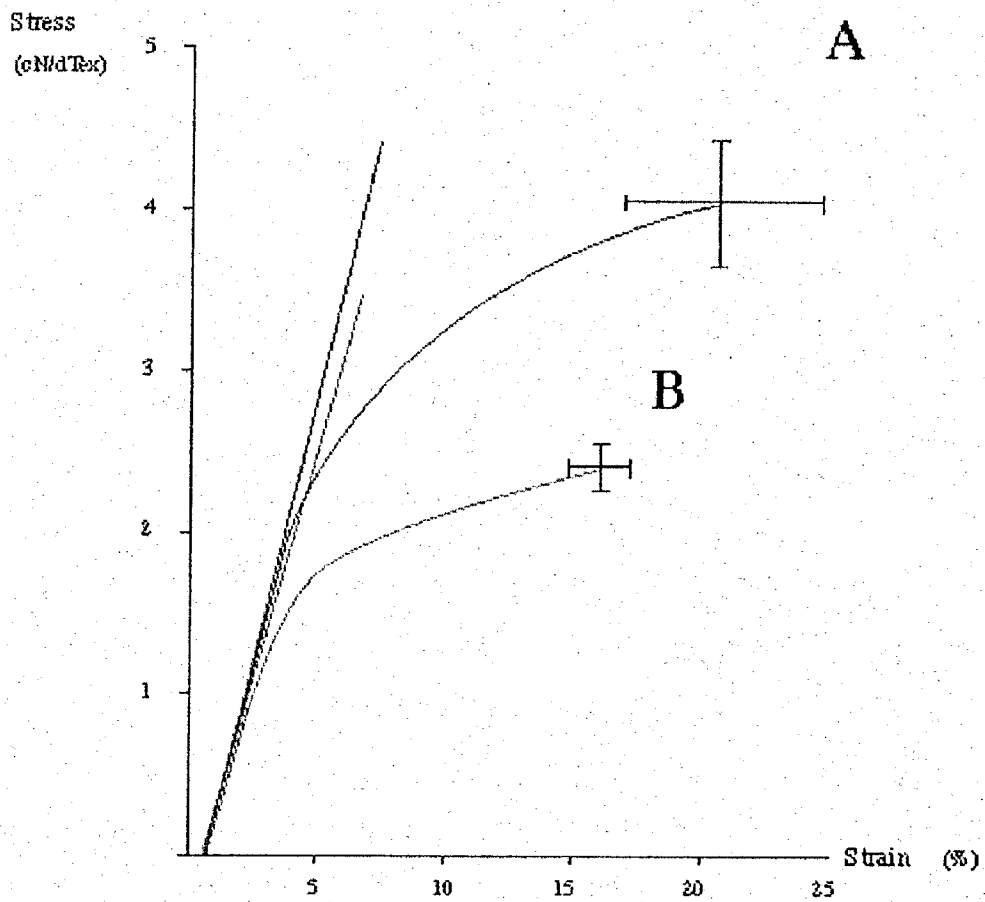


Figure 5



A:mori silk fiber, B:A stress/distortion curve of regenerated silk fiber obtained from HFA system

1)"Textile & Material", Pressed by Japanese Material Chemistry Org., 178(1991)

2)"Structure of Silk Fiber : 2nd Version" Ed. By Nobumasa Honjyo Pressed by Shinshu University 1980

Figure 6

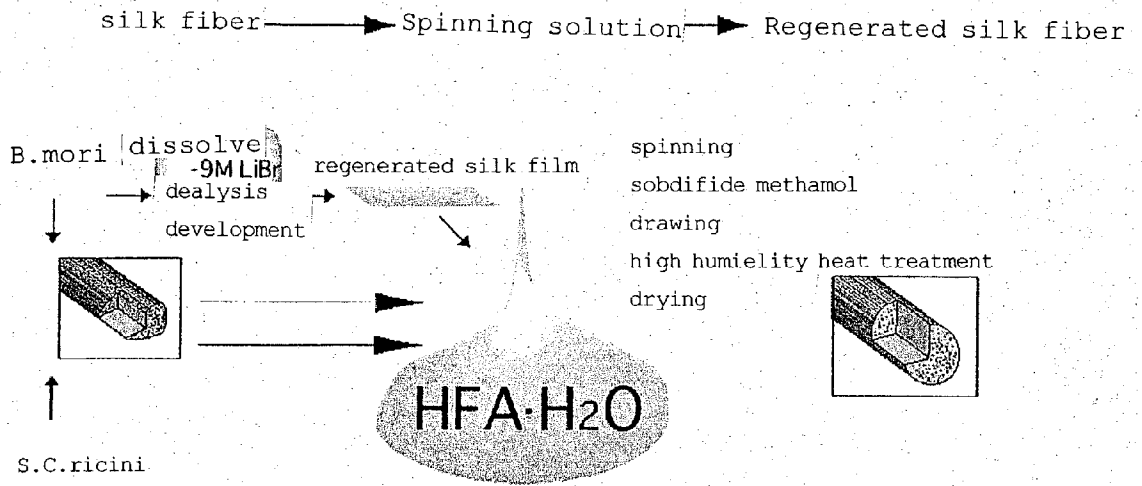


Figure 7

METHOD OF PRODUCING FIBER AND FILM OF SILK AND SILK-LIKE MATERIAL

FIELD OF THE INVENTION

[0001] This invention relates to a method of manufacturing silk, silk fibers or film, and silk-like fibers or film. More specifically this invention relates to a method of manufacturing silk fibers or film, and silk-like fibers or film using hexafluoroacetone hydrate as a solvent.

BACKGROUND OF THE INVENTION

[0002] In recent years, with progress in biotechnology, many attempts are being made to produce silk-like materials having various functions using intestinal bacteria, yeast, or animals such as goats. For this purpose, suitable solvents are required to make it possible to produce fibers or films from raw silk materials. For both *B. mori* fibers and wild silkworm fibers, excellent solvents are also required to produce single thread fibers.

[0003] In the previous works, hexafluoroisopropyl alcohol (HFIP) was often used to obtain regenerated *B. mori* silk fibers which did not induce decrease of molecular weight and had excellent mechanical properties (U.S. Pat. No. 5,252,285). As natural *B. mori* silk fibers cannot dissolve in HFIP, the fibers are first dissolved in an aqueous solution of a salt such as lithium bromide, which is removed during dialysis: after drying, the silk fibroin prepared as a film form is dissolved in HFIP. However, 8 days are required until complete dissolution of silk film in HFIP (U.S. Pat. No. 5,252,205).

[0004] Further, silk fibers from wild silkworms such as *S. c. ricini* are insoluble in HFIP. The inventor therefore carried out research on the compatibility of solvents for silk fibroins, and attempted to find out solvents superior to HFIP. As a result, it was found that hexafluoroacetone hydrate (hereafter referred to as HFA) is an excellent solvent for producing fibers and films from raw silk materials.

[0005] Specifically, the conditions required of such a solvent for silk fibroins are:

[0006] (1) It must destroy strong hydrogen bonds among silk fibroin chains,

[0007] (2) It must dissolve the silk fibroins within a short time,

[0008] (3) It must dissolve the silk fibroins without decomposing the silk fibroin chain,

[0009] (4) The silk fibroin solutions must be stable for long time,

[0010] (5) The solution must have sufficient viscosity for spinning,

[0011] (6) The solvent should not remain after the silk fibroins have solidified, that is, the solvent should be easily removable.

[0012] HFA satisfies all these conditions, and can also dissolve the silk fibers from wild silkworms.

[0013] It is therefore a first object of this invention to provide a method of manufacturing fibers or films of silk and/or silk materials without decomposition.

[0014] It is a second object of this invention to provide a method of manufacturing fiber or film from silk fibroins of wild silkworms.

DISCLOSURE OF THE INVENTION

[0015] The above objects of this invention are attained by a method wherein silk or silk fibers are manufactured by spinning them from a solution wherein silk fibroins and/or silk materials are dissolved in hexafluoroacetone hydrate or a solvent system having this as the main component, and extruded if necessary. They are also attained by a method wherein silk or a silk film is manufactured by developing on a support a solution wherein silk fibroins and/or silk materials are dissolved in hexafluoroacetone hydrate or a solvent system having this as its main component, drying, and extruding if necessary.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] A in FIG. 1 is a formula of hexafluoroacetone used as a spinning solvent in this invention. B in FIG. 1 is a formula of a diol from which reacted with a water molecule, and C is the reaction equation.

[0017] FIG. 2 is a solution ^{13}C NMR spectrum of *B. mori* fibroin in HFA hydrate.

[0018] FIG. 3 is a solid-state ^{13}C CP/MAS NMR spectrum of *B. mori* silk fibroin fibers regenerated from the HFA solution.

[0019] A in FIG. 4 is an X-ray diffraction pattern of silk fibroins regenerated from the HFA solution, and B is an X-ray diffraction pattern of the natural silk fibroin fibers.

[0020] A in FIG. 5 is a DSC diagram of a sample wherein silk fibroins regenerated from the HFA solution after heat-treating at 100°C ., and B is a DSC diagram of the sample after heat-treating at 125°C .

[0021] A in FIG. 6 is a stress-strain curve of the natural silk fibroin fibers, and B is a stress-strain curve of silk fibroin fibers regenerated from the HFA solution.

[0022] FIG. 7 is a diagram describing the regeneration of the silk fibroin fibers from the HFA solution.

PREFERRED EMBODIMENTS OF THE INVENTION

[0023] The hexafluoroacetone used in this invention is the substance shown in A of FIG. 1, and is normally present in a stable state as a hydrate. Therefore, the hydrate is used also in this invention. There is no particular limitation on the hydration number. In this invention, depending on the characteristics of the silk materials, the HFA may also be diluted with water or with HFIP. In this case, it is also desirable that at least 80% of the mixture is HFA. According to this specification, the solvent which is diluted in this way is referred to as a solvent having HFA as its main component.

[0024] The silk fibroins used in this invention refer to silk fibroins from silkworms such as *B. mori*, *S. c. ricini*, *A. pernyi* and *A. yamamai*. Silk materials mean proteins as, for example, represented by the general formula $-(\text{GA}^1)_k-$, $((\text{GA}^2)_k-\text{G}-\text{Y}-(\text{GA}^3)_1)_m$, or $[\text{GGAGSGYGGGYGH-GYGSDDGG}(\text{GAGAGS})_3]_n$. G is glycine, A is alanine, S is serine and Y is tyrosine. The former is described in detail in Patent Application 2000-84141. A^1 in the above general formula is alanine, and every third A^1 may be serine. A^2 and A^3 are both alanine, and part thereof may be valine.

[0025] In this invention, the silk fibroins and/or silk-like materials may be dissolved in exclusively HFA. It should be mentioned that in the case of the HFIP, *B. mori* fibers and wild silkworm fibers could not be dissolved. Also, as in the case of HFIP, the silk fibers may first be dissolved in LiBr, dialyzed to remove LiBr and developed on a support to form a film, and the film obtained may then be dissolved in HFA. The solubility in this case is much better than those of HFIP. The operability is largely improved, and the mechanical properties of the fibers are also better than those obtained with HFIP as a solvent. It is also possible to use a mixture of HFA and HFIP as a solvent in this invention. In this case, the relative proportion of the two may be determined according to the proteins which it is desired to dissolve.

[0026] According to this invention, the silk fibroin film is dissolved in hexafluoroacetone hydrate, so there is almost no possibility of the decomposition of the silk fibroin chain, and the silk solution can be obtained within a shorter time than in the previous case, HFIP. Further, if longer dissolution time is possible, *B. mori* fibers can be directly dissolved without preparing a film, wild silkworm fibers such as *S. c. ricini* and *A. yamamai* can be directly dissolved, and the regenerated silk fibers or films can be obtained.

[0027] This invention will now be described in further detail by specific examples, but it should be understood that the invention is not be construed as being limited by these examples in anyway.

EXAMPLES

Example 1

[0028] Spring cocoon, 1999, Shunrei x Shogetsu was used as the *B. mori* cocoon. The sericin protein or other fats which cover the fibroins are removed by degumming. The degumming method is as follows.

[0029] Degumming Method

[0030] A 0.5 wt % aqueous solution of a Marseille-soap (No. 1 Chemical Industries) was prepared, and heated to 100° C. The cocoon layer mentioned above was introduced, and after manipulating the fibers, the solution was boiled with stirring. After boiling for 30 minutes, these fibers were rinsed in distilled water heated to 100° C. This operation was repeated 3 times. The fiber was boiled for a further 30 minutes with distilled water, rinsed and dried to give silk fibroins.

[0031] As mentioned above, *B. mori* fibroins are soluble in HFA in the form of fibers. However, it requires at least 2 months for complete dissolution.

[0032] Therefore, to make it dissolve more quickly, a regenerated *B. mori* fibroin film was produced as follows, and used as a sample.

[0033] Production of Regenerated *B. mori* Silk Fibroins

[0034] To dissolve *B. mori* silk fibroin fibers, an 9M aqueous solution of LiBr was used. The 9M LiBr aqueous solution of silk fibroins obtained was filtered under reduced pressure using a glass filter (3G2) to remove the residue in the aqueous solution.

[0035] Then, a permeable membrane made from cellulose (VISKASE SELES CORP, Seamless Cellulose Tubing, 36/32) was used for dialysis for four days against distilled water to remove LiBr.

[0036] The aqueous solution of the silk fibroin was poured on a plastic plate (Eiken Equipment Inc., sterile, square No. 2 Petri dish), allowed to stand for two days at room temperature to obtain a regenerated *B. mori* fibroin film.

[0037] The concentrations of the silk fibroin and the dissolution rates were examined (Table 1) using HFA.3H₂O (Aldrich Chem. Co.) as a spinning solvent.

[0038] The thickness of the film was about 0.1 mm. HFA.3H₂O tends to evaporate and therefore, the film was dissolved at 25° C. without heating.

[0039] In the case of this example, it was found that the silk fibroin concentration which is suitable for spinning is 8 to 10 wt %. Moreover, it was found that at this concentration, the dissolution time was very short, e.g., 2 hours.

[0040] HFA has different hydrates. In this example the trihydrate and x hydrate were used, but no difference was found in the solubility.

[0041] *B. mori* silk fiber could be dissolved directly in HFA (silk fibroin concentration is 10 wt %) without forming as film, but the dissolution took two months or more.

TABLE 1

Dissolution concentration and dissolution rate of <i>B. mori</i> fibroin		
Silk concentration in solution (%)	Dissolution time (hours)	State
3	within 0.2	Δ
5	within 0.2	○
8	1	⊙
10	2	⊙
15	2	○
20	within 48	Δ
25	—	x

⊙: Concentration excellent for spinning

○: Concentration satisfactory for spinning

[0042] The silk fibroin film was placed in HFA, stirred and allowed to stand at 25° C. to dissolve it. Then the solution was degassed to give a spinning stock solution. A cylinder was filled with the spinning stock solution, and this was spun into a bath from a nozzle of diameter 0.45 mm to coagulate it.

[0043] The results on the coagulant solvents in the bath which coagulates the sample are shown in Table 2.

[0044] From these results, 100% methanol was used as the coagulant solvent in the bath, and fibers which were allowed to stand in this bath overnight, were used as non-stretched sample.

TABLE 2

Optimum coagulate solvent	
Coagulant solvent	Result
100% methanol	⊙/high transparency
100% ethanol	○/low solidifying properties
100% acetone	Δ/whitening

⊙: Best for spinning

○: Good for spinning

Δ: Unsuitable for spinning

x: Spinning impossible

[0045] When the non-stretched samples were stretched during soaking in 100% methanol or water, it showed high

elasticity at room temperature. If it was dried immediately after immersion without stretching, the strength and elasticity of the sample were remarkably low. The reason why water was chosen as coagulant solvent in the bath is that the operability is good. The largest stretching ratio of the fiber from the HFA solution was 4 times, and the averaged stretching ratio was about 3 times.

[0046] After stretching, the samples pulled up from the water into the air were shrunk. To prevent this shrinkage, it was heat-treated using 125° C. steam in an autoclave (Tommy Inc. Precision Instruments, AUTOCLAVE SS-325) and the silk sample was fixed with the drawing machine during the treatment. In spite of such a heat treatment, the sample still shrunk in the drying process. Therefore, it was dried at room temperature by fixing the sample with drawing machine to give the silk fiber. The above conditions are summarized in Table 3.

TABLE 3

Manufacturing of regenerated <i>B. mori</i> silk fibers from HFA solution		
<u>Spinning</u>		
Spinning sample:	sample	<i>B. mori</i> silk fibron fibers
	form of sample	
Spinning method:	wet spinning	
Spinning solution:	solvent	HFA-H ₂ O
	silk fibron concentration (weight %)	10
	dissolution temperature (° C.)	25
	dissolution time	within 1 day
Spinning nozzle:	spinning nozzle diameter (mm)	0.2
	spinning nozzle length (mm)	1.2
Coagulation:	coagulant solvent	methanol
	coagulation bath temperature (° C.)	20
	spinning rate (g/min)	0.48
	drawing ratio (times)	1.62
<u>Treatment after spinning:</u>		
removal of spinning solvent:	temperature (° C.)	24
	time	1 night
stretching:	stretching	in water
	stretching temperature (° C.)	24
	stretching ratio (times)	1.77
high humidity heat treatment:	temperature (° C.)	125
	time (min)	30
drying:	temperature (° C.)	24

[0047] For producing a large amount of samples, the series of above steps were performed to obtain a regenerated silk fiber using two types of monofilament production apparatus (Toshin Industries Inc.), and a nozzle from Kasen Nozzles Co.

[0048] After these process, it was found that a regenerated silk fiber having very few breaks together with excellent spinning stability and stretching stability can be obtained steadily and continuously.

[0049] Viscosity Measurement of Spinning Stock Solution

[0050] The viscosity measurement was performed for silk fibron/HFA (silk concentration of 10 wt %), which was used as a spinning stock solution with continuous spinning.

[0051] A mechanical spectrometer (Rheometric Far East. Ltd., RMS-800) was used for the measurement. The frequency dependence was measured when the distortion was rad 50%. The viscosity was measured by changing the frequency. This shear rate was extrapolated to 0, and the 0 shear viscosity was calculated. As a result, the viscosity of the spinning stock solution was 18.32 poise.

[0052] ¹³C Solution NMR Measurement

[0053] In order to perform structural analysis of *B. mori* fibron in the spinning stock solution, ¹³C solution NMR measurements were performed. For this purpose, a JEOL alphaS500 spectrometer was used. Measurements were performed at a pulse interval of 3 seconds, scanning number of 12,000 and temperature of 20° C. The silk fibron in HFA-xH₂O (3%) was observed.

[0054] As shown in FIG. 2, it is clear that decomposition of the chain did not occur in the HFA-xH₂O. From the chemical shifts of the main peaks from alanine of *B. mori* silk fibron, it was clear that *B. mori* fibron took an alpha helix structure. Moreover, from the ¹³C solution NMR measurement, the HFA hydrate exists as a diol form (B and C in FIG. 1).

[0055] Hence, the silk fibron has a different structure in solution from that in HFIP which is also a fluorinated alcohol.

[0056] On the other hand, from the ¹³C CP/MAS spectrum, the structure of the film from the spinning solution is in an alpha helix, and a large amount of HFA still remained.

[0057] ¹³C CP/MAS NMR Measurement

[0058] A Chemagnetic CMX400 spectrometer was used for the ¹³C CP/MAS NMR measurements. The C alpha and C beta regions are expanded in FIG. 3. It was clear that an alpha helix was formed in the regenerated film from the spinning stock solution, and a beta sheet was formed in the regenerated *B. mori* silk fibers. This shows that a structural transition occurred due to spinning.

[0059] HFA-xH₂O was added to *B. mori* silk fiber to dissolve it. Subsequently, C alpha and C beta peaks were observed in the dried material and the film from the spinning stock solution. From this, it is seen that HFA remains in *B. mori* fibron sample, and that it cannot be removed only by drying. Further, although the strength is less than that of the former material, the peaks from HFA were observed even in a non-stretched regenerated silk fiber which had only been spun. This shows that HFA is not completely eliminated merely by spinning out into the coagulate solvent like the case of the reproduced silk fiber from the HFIP solution.

[0060] Wide-Angle X-Ray Diffraction Measurements

[0061] A regenerated silk fiber (3 times stretching ratio) obtained by continuous spinning was used for observation with wide-angle X-ray diffraction. For the measurement, Cu was used as the target under the conditions of 40 Kv, 100 mA using a Rigaku Denki, Inc. RINT-2400 rotating target X-ray diffraction machine. From the default pattern in the equatorial direction, a diffraction peak in the vicinity of 2theta= 20 degrees close to the x-ray diffraction pattern for *B. mori* silk fibers appeared, showing that a beta sheet structure is formed. FIG. 4 shows that the peak due to the orientation in

the azimuth angle direction at 19.8 degrees was observed together with the case of *B. mori* silk fibers.

[0062] Any difference was not observed about the orientation between the silk fibers from the HFA solution and *B. mori* silk fibers. This indicates that the crystal size of beta sheet crystals and the orientation of the regenerated silk fiber are sufficient. FIG. A shows regenerated silk fibroin fibers and FIG. B shows natural silk fibroin fibers.

[0063] DSC Analysis

[0064] The sample for DSC measurement was prepared by filling the regenerated silk fibers in an aluminium pan, and filling with N₂ gas. The samples were cut to approximately 5 mm. The apparatus was a Rigaku Denki THERMOFLEX (DCS 83 230D). The temperature range was 30-350° C., and the rate of temperature rise was 10° C./minute. The DSC curve of the regenerated silk fibers from the HFA solution is shown in FIG. 5. The heat absorption peak appearing in the vicinity of 70-80° C. is probably due to the vaporization of moisture absorbed in the sample.

[0065] FIG. 5 shows the curve of regenerated silk fibers at a different high humidity and heat processing temperature. An exothermic peak appears at 123° C. in the curve of a specimen manufactured at a processing temperature of 100° C. (FIG. 5A). As the peak does not appear in the curve of regenerated silk fibers using HFIP as solvent, it suggests that HFA acts strongly on the silk fibroins, and crystallization does not go to completion during the period from solidification to stretching. This exothermic peak was in a low

which were heat-treated at 125° C. indicate similar results. Further, the melting temperature and their thermal capacity showed excellent values compared to the regenerated silk fibers from HFIP solution. From these facts, it can be postulated that crystallization of amorphous and crystal components was made possible by effective heat treatment. This fact does not contradict the results of ¹³C CP/MAS analysis and the results of the tensile strength.

[0067] Tensile Strength

[0068] The sample was a specimen piece of 70 mm, sandpaper grip 10 mm and grip interval 50 mm. For the measurement, a Tensilon (Shimazu Labs. Inc, AGS-10 kg) was used. The rate of elongation was fixed, and the cell was a 10 Newton cell. Measurement was performed at a cross-head speed of 50 mm/min referring to JIS L-0105, L-1069, L-1095 and ASTM D 2101, D 2258.

[0069] Young's modulus, tensile fracture strength and extension were determined from the stress-strain curve obtained by measuring the regenerated silk fibers from HFA solution. The averaged values over 10 experiments were obtained. The results are summarized in Table 4 and FIG. 6. As a result, it was found that the stress-strain curve of the regenerated silk fibers had a similar shape to that of *B. mori* silk fibers, and that these fibers had a suitable strength, elasticity and extension for practical use. Further, the superior fibers obtained had a similar or better extension and strength than the regenerated silk fibers from HFA solution. Further, the fibers were extremely uniform, and there was very little discrepancy in the strength or extension.

TABLE 4

<i>B. mori</i> silk fibers regenerated from the HFA solution			Measurement of tensile strength and elongation		
Sample	Elongation factor (times)	diameter (μm)	maximum tensile elongation	maximum tensile strength (%)	Young's modulus
<i>B. mori</i> silk fibers produced from the HFA solution	3.00* ¹	43	2.18(2.02-2.31)(cN/dTex) 0.29(Gpa)	15.6 (12.8-16.6)	74.0(68.4-78.9)(cN/dTex)
<i>B. mori</i> silk fibers	3.00* ²	—	1.92(1.78-2.04)(gf/d) 1.63(cN/dTex) ± 0.19 1.44(gf/d) ± 0.19	17.3 ± 4.3	65.3(60.4-69.6)(gf/d)
	—	approx. 15	0.39(Gpa)	16.5	

*¹Heat treatment temperature: 125° C.

*²Heat treatment temperature: 100° C.

temperature region which does not appear in previous peaks from *B. mori* silk fibroins. However, regarding the ¹³C CP/MAS NMR measurement, the peak pattern is substantially identical to that for *B. mori* silk fibers, so it is seen that crystallinity improves due to the strong action of HFA. Also, it is postulated that, in *B. mori* silk fibers, crystallization occurs in the crystalline region.

[0066] If crystallization occurs in the crystal region which was disordered to some extent at 123° C., it suggests that, by setting the heat treatment temperature higher than this to promote crystallization, there would be a large effect on the mechanical properties. Therefore, the processing temperature was set to 125° C., and a DSC measurement was performed on the regenerated silk fibers. As a result, the above peak did not appear (FIG. 5B). The melting temperature of highly oriented silk fibers appears at 300° C. or above, and the regenerated silk fibers from HFA solution

[0070] From the above results, it was confirmed that *B. mori* silk fibers could be directly dissolved in HFA hydrate. However, two months or more are required for the dissolution. Therefore, it is preferred to dissolve the fibers in an aqueous solution of LiBr and remove the LiBr by dialysis against water. After drying, silk film was obtained and then it was dissolved in HFA hydrate. In this case, the concentrations of 8 -10 wt % are suitable for the spinning. Thus, there is much better process than the case of HFIP system. HFA had a superior effect in cleaving the strong intramolecular and/or inter-molecular hydrogen bonds of *B. mori* silk fibroins.

[0071] As the spun fibers do not easily break, it appears that HFA hydrate does not interfere the orientation of molecular chains or the formation of intra-molecular and/or inter-molecular hydrogen bonds. Also, these fibers had much less shrinkage than the regenerated silk fibers from the HFIP

solution. Further, the ¹³C CP/MAS and DSC measurements show that the crystal orientation in the stretched silk fibers (x 3 times) which were heat-treated at 100° C. is incomplete. When the heat treatment was performed at 125° C., it was discovered that the fibers had an equivalent orientation to that of *B. mori* silk fibers. The highest crystal melting points of all three systems were obtained, and a high crystal stability was observed.

[0072] It was found that the dynamic physical properties of the regenerated silk fibers were of the same order of, or superior to, those of HFIP regenerated silk fibers. Also, from the fact that the fibers obtained were extremely uniform, it was conjectured that the silk fibroins were dissolved in HFA uniformly, and was present without interfering with structural transitions occurring during spinning. A scheme of regenerated silk fiber from the HFA solution is shown in FIG. 7.

[0073] Manufacturing of Regenerated *S. c. Ricini* Silk Fibers

[0074] Cocoons produced at 1997 year were used as the starting material. This was carefully disentangled with tweezers.

[0075] The sericin proteins and other lipids covering the fibroins were removed by degumming to obtain the silk fibroins. The degumming method was as follows.

[0076] Degumming Method

[0077] A 0.5 wt % aqueous solution of sodium bicarbonate (NaHCO₃) (Wako Pure Chemical Industries, Inc., special grade) was prepared and heated to 100° C. The cocoon was introduced and the solution was boiled with stirring. After 30 minutes, the cocoons were rinsed in distilled water at 100° C. This operation was repeated 5 times and the cocoons were boiled again for 30 minutes in distilled water, rinsed, and then dried to give the silk fibroins.

[0078] The concentration of silk fibroins in the solvent and their dissolution rate were examined using HFA.xH₂O (Tokyo Chemical Industries,) (Table 5). The most suitable concentration of silk fibroins in this experiment was 10 wt %. The silk fibroin/HFA.xH₂O solution was a light yellow color. HFA.xH₂O has a low boiling point and high volatility, so the solution was prepared at 25° C. without heating. After the silk fibroins were mixed with the spinning solvent and stirred, they were stand at 25° C. to dissolve the silk fibroins, and fully degassed to give a spinning stock solution.

TABLE 5

Dissolution concentration and dissolution rate of <i>S. c. ricini</i> fibroin		
Silk concentration in solution (%)	Dissolution time (hours)	State
8	within 2 days	Δ
10	5 days	○
12	10 days or more	x

○: Concentration satisfactory for spinning
 Δ: Concentration unsuitable for spinning
 x: Spinning impossible

[0079] The spinning solution was filled in a cylinder, and spun out into a coagulant bath from a nozzle of diameter 0.45 mm. FIG. 6 shows the results of examining the coagulation. From this, it is seen that it was difficult to obtain fibers of identical transparency to those of *B. mori*. This difference seems due to the primary structure. Using 30%

ethanol/acetone as the coagulation bath, which has a comparatively high fiber-forming capacity, the spun fibers were left in the coagulation bath overnight and were used as a non-stretched sample.

TABLE 6

Optimum component conditions for coagulant solvent	
Coagulant solvent	Result
100% methanol	Δ/whitening
90% methanol/water	Δ/whitening
80% methanol/water	Δ/whitening
75% methanol/water	x/low coagulation properties
70% methanol/water	x/low coagulation properties
85% methanol/ethanol	Δ/low coagulation properties
70% methanol/ethanol	Δ/low coagulation properties
10% methanol/ethanol	Δ/whitening
5% methanol/ethanol	Δ/low coagulation properties
2% methanol/ethanol	Δ/low coagulation properties
100% ethanol	Δ/low coagulation properties
90% ethanol/water	Δ/low coagulation properties
90% ethanol/acetone	Δ/low coagulation properties
40% ethanol/acetone	Δ/whitening
30% ethanol/acetone	Δ/whitening
17% ethanol/acetone	Δ/whitening
100% acetone	Δ/whitening

Δ: Unsuitable for spinning
 x: Spinning impossible

[0080] Stretching Conditions

[0081] As a result of stretching studies, it was found that the average stretching ratio was 1.7 times. Compared to *B. mori* regenerated silk fibers, the stretching rate was low. From the above results, it is clear that, by direct addition of HFA.xH₂O to *S. c. ricini* silk fibroin fibers, a solution having a suitable viscosity for spinning can easily be manufactured.

[0082] The silk concentration which gave a suitable viscosity for spinning was 10 wt %. The non-stretched fibers did not have good stretching stability, and breaks of the fibers occurred.

[0083] Industrial Advantage of the Invention

[0084] As described above, by using HFA, regenerated silk fibers and synthetic silk fibers could not only be manufactured more easily than in the prior art, but could also be made into a film by varying the thickness. Therefore, this remarkably extends the application field of silk and silk-like materials.

What is claimed is:

1. A method of manufacturing silk or silk fibers spun from a solution in which silk fibroins and/or silk materials are dissolved in hexafluoroacetone hydrate or a solvent having this as its main component, and extending them if necessary.

2. The method of manufacturing silk or silk fibers as defined in claim 1, wherein a film is manufactured from an aqueous solution wherein silk fibroins and/or silk materials are dissolved in lithium bromide, the lithium bromide is removed by dialysis, and the film is then dissolved in hexafluoroacetone hydrate or a solvent having this as its main component.

3. A method of manufacturing silk or a silk film, wherein a solution in which silk fibroins and/or silk materials are dissolved in hexafluoroacetone hydrate or a solvent having this as its main component is developed on a support, and then extended after drying if necessary.

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